

Measurement of Thermal Diffusivity of Anisotropy Graphite Sheet Using Laser-Heating AC Calorimetric Method¹

H. Nagano^{2, 6}, H. Kato³, A. Ohnishi⁴ and Y. Nagasaka⁵

- ¹ Paper presented at the Fourteenth Symposium on Thermophysical Properties, June 25-30, 2000, Boulder, Colorado, U.S.A.
- ² Graduate School of Science and Technology, Keio University, 3-14-1, Hiyoshi, Yokohama 223-8522, Japan.
- ³ National Research Laboratory of Metrology, 1-1-4, Umezono, Tsukuba, Ibaraki 305-8563, Japan.
- ⁴ Institute of Space and Astronautical Science, 3-1-1, Yoshinodai, Sagamihara, Kanagawa 229-8510, Japan.
- ⁵ Department of System Design Engineering, Keio University, 3-14-1, Hiyoshi, Yokohama 223-8522, Japan.
- ⁶ To whom correspondence should be addressed.

ABSTRACT

The thermal diffusivity of graphite sheet having extremely large anisotropy has been measured by a laser heating ac calorimetric method in the temperature range from 30 to 350 K. This graphite sheet has characteristics of high thermal diffusivity, large anisotropy and thinness, and so it is difficult to apply conventional ac technique. Therefore, we propose the simultaneous measurement method for the in-plane and the out-of-plane thermal diffusivities, by analyzing the three-dimensional heat conduction process, which contains the effects of anisotropy and thermal wave reflections. This method was verified by checking with the thermal diffusivities of isotropic materials such as stainless steel and pure copper, and was applied to the anisotropic thermal diffusivity measurement of the graphite sheet.

KEY WORDS: anisotropy; graphite sheet; high thermal diffusivity; laser-heating ac calorimetric method; simultaneous measurement.

1. INTRODUCTION

We have proposed a high thermal conductive graphite sheet (GS) for the spacecraft thermal control application. The GS, which has been developed by Matsushita Electric Industrial Co., Ltd., is two-dimensional orthotropic material. We have measured both the in-plane and the out-of-plane thermal diffusivity by a laser-heating ac calorimetric method [1 - 3]. In the present ac technique, a modulated laser beam, which is focused, is irradiated upon a sample surface, and the phase-lag of thermal wave is detected by a fine thermocouple [4]. In-plane thermal diffusivity is determined by the slope of the relation of the phase-lag vs. relative distance between heating point and the detection point, and out-of-plane thermal diffusivity is calculated by the phase-lag vs. modulating frequency.

In the case of GS measurement, the following feature of GS must be taken into account:

(1) GS has high thermal diffusivity in the in-plane direction.

If the thermal diffusivity of the sample is high, the measured thermal diffusivity significantly deviates from the correct one due to the effects of the thermal wave reflections at the edges of the sample. Gu *et al.* [5] reports the theoretical consideration of effect of the first reflection at the edge in the light scanning direction (x direction). However, in the present system, we need to consider the reflections in several directions, repeatedly due to high thermal diffusivity of GS.

(2) GS is thin material (100 μm in thickness).

In a thin sample, the size of the silver paste to attach the thermocouple to the sample becomes relatively larger, and resulting in the contribution to the phase-lag measurement. Hatta *et al.* [6] reports there is no effect of the silver paste on the

in-plane measurement because the heat capacity of the silver paste does not affect on the slope of the phase-lag vs. distance. However in the out-of-plane measurement, the effect of silver paste cannot be neglected because the degree of the effect of silver paste is changed in accordance with the modulating frequency. Therefore, by an ac technique, the out-of-plane thermal diffusivity measurement has been limited to poor thermal diffusive material or/and thick material [7].

In the present paper, we propose a new method to determine both the in-plane and the out-of-plane thermal diffusivity, simultaneously by analyzing the three-dimensional heat conduction process, which contains the effects of thermal wave reflections and anisotropic thermal diffusivity. The three-dimensional ac temperature response for an anisotropy plate-like sample is numerically estimated using Green's function. The applicability of the simultaneous method to ac technique was tested at room temperature by using isotropic materials such as stainless steel and pure copper. In addition, this method was applied to the anisotropic thermal diffusivity measurement of the graphite sheet in the temperature range from 30 to 350 K.

2. THEORETICAL ANALYSIS

First of all, consider a homogeneous medium of three-dimensional infinite extent. When a point heat source is liberated at the rate $\mathbf{r}ce^{i\omega t}$ at the point (x', y', z') , where \mathbf{r} is the average density of the media and c the heat capacity, the propagation of thermal waves in a three-dimensional infinite region can be expressed as [8],

$$T_{ac}(x, y, z, t) = \frac{1}{4\pi \mathbf{r} a l(x, y, z)} \cdot \exp[-kl(x, y, z) + i\{\omega t - kl(x, y, z)\}], \quad (1)$$

where T_{ac} is the ac temperature at the detection point (x, y, z) , $\omega = 2\pi f$ the angular frequency, and a the thermal diffusivity. l is the distance between the heat source and the detection point and can be written as,

$$l(x, y, z) = \sqrt{(x - x')^2 + (y - y')^2 + (z - z')^2}. \quad (2)$$

k is the thermal wave number defined as,

$$k = \sqrt{\frac{\omega}{a}} = m^{-1}, \quad (3)$$

where m is the thermal diffusion length. The detected phase-lag $\Delta\phi$ of the thermal wave is given by,

$$\Delta\phi(x, y, z) = -kl(x, y, z). \quad (4)$$

Secondly, consider a three-dimensional orthotropic medium of three-dimensional infinite region. Green's function at x at the time t due to the unit instantaneous heat source at x' at the time t' is,

$$G_x(x, t; x', t') = \frac{1}{2\sqrt{\pi a_x(t-t')}} \left\{ \exp\left(-\frac{(x-x')^2}{4a_x(t-t')}\right) \right\}, \quad (5)$$

where a_x is thermal diffusivity in the x direction. Green's functions at y and z

can be written as the same configuration with thermal diffusivities a_y and a_z . The ac temperature response is written as,

$$\begin{aligned}
 T_{ac}(x, y, z, t) &= \int_{-\infty}^t e^{i\omega t'} \cdot G_x(x, t; x', t') \cdot G_y(y, t; y', t') \cdot G_z(z, t; z', t') dt' \\
 &= \frac{e^{i\omega t}}{4p\sqrt{a_y a_z} l'(x, y, z)} \exp[-k_x l'(x, y, z) + i\{\omega t - k_x l'(x, y, z)\}],
 \end{aligned} \tag{6}$$

where

$$l'(x, y, z) = \sqrt{\frac{a_x}{a_x}(x-x')^2 + \frac{a_x}{a_y}(y-y')^2 + \frac{a_x}{a_z}(z-z')^2}, \quad k_x = \sqrt{\frac{p f}{a_x}}. \tag{7}$$

Lastly, let us consider three-dimensional orthotropic medium of the semi-infinite region shown in Fig. 1 (a), with a width w along the y axis, a thickness d along the z axis and infinite length along the x axis, where the length is longer enough than the scanning length and thermal diffusion length. The detected ac temperature is a sum total of the thermal wave propagated from the point heat source directly, and the waves, which are reflected at the edges of the sample and then reaches the detection point. When the point heat source is located at (x', y', z') , the thermal wave in the y direction is reflected at $(x', y' \pm w/2, z')$. Furthermore, thermal waves are reflected repeatedly at reciprocal edges. One can consider these reflected waves as thermal waves propagated from imaginary heat source at $(x', y' \pm mw, z')$ as shown in Fig.1 (b) [9]. The same assumption is adapted to the z direction as shown in Fig. 1 (c). The Green's function in the z direction is expressed as,

$$\begin{aligned}
G_z(z, t; z', t') = & \frac{1}{2\sqrt{\mathbf{p}a_z}(t-t')} \left[\exp\left(-\frac{(z-z')^2}{4a_z(t-t')}\right) + \exp\left(-\frac{(z+z')^2}{4a_z(t-t')}\right) \right] \\
& + \frac{1}{2\sqrt{\mathbf{p}a_z}(t-t')} \left[\sum_{n=1}^{\infty} \mathbf{g}^{2n-1} \left\{ \exp\left(-\frac{[z-(z'+2nd)]^2}{4a_z(t-t')}\right) + \exp\left(-\frac{[z+(z'+2nd)]^2}{4a_z(t-t')}\right) \right\} \right] \\
& + \frac{1}{2\sqrt{\mathbf{p}a_z}(t-t')} \left[\sum_{n=1}^{\infty} \mathbf{g}^{2n} \left\{ \exp\left(-\frac{[z-(z'-2nd)]^2}{4a_z(t-t')}\right) + \exp\left(-\frac{[z+(z'-2nd)]^2}{4a_z(t-t')}\right) \right\} \right]
\end{aligned} \quad (8)$$

where \mathbf{g} is thermal wave reflectance at the ample-exterior interface defined by [10],

$$\mathbf{g} = \frac{e_s - e_e}{e_s + e_e}, \quad (9)$$

where e_s and e_e are thermal effusivities of the sample and the exterior, respectively.

When the laser beam is irradiated at the point (0, 0, 0), the ac temperature response is written as,

$$\begin{aligned}
T_{ac}(x, y, z, t) = & \frac{e^{i\omega t}}{4\mathbf{p}\sqrt{a_y a_z}} \left[2 \frac{e^{-(1+i)kl''(0,0)}}{l''(0,0)} + 2 \sum_{m=1}^{\infty} \mathbf{g}^m \left\{ \frac{e^{-(1+i)kl''(m,0)}}{l''(m,0)} \right\} \right. \\
& \left. + \sum_{n=1}^{\infty} \mathbf{g}^{2n-1} (\mathbf{g}+1) \left\{ \frac{e^{-(1+i)kl''(0,n)}}{l''(0,n)} \right\} + \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \mathbf{g}^{2n+m-1} (\mathbf{g}+1) \left\{ \frac{e^{-(1+i)kl''(m,n)}}{l''(m,n)} \right\} \right],
\end{aligned} \quad (10)$$

where

$$l''(m, n) = \sqrt{x^2 + \frac{a_x}{a_y} (mw)^2 + \frac{a_x}{a_z} [(2n+1)d]^2}. \quad (11)$$

In the present measurement system, the experiment is performed in a vacuum, and so the thermal wave reflectance g is equal to 1. Additionally, GS is two-dimensional orthotropic material, and has homogeneous structure in $x-y$ directions (i.e. $a_x = a_y \equiv a_{xy}$). The phase-lag detected at $(x, 0, d)$ is obtained from,

$$Df(x, y, z) = \tan^{-1} \frac{\sum_{n=0}^{\infty} \left\langle \left[\frac{e^{-kl''(0,n)}}{l''(0,n)} \sin\{kl''(0,n)\} \right] + 2 \sum_{m=1}^{\infty} \left[\frac{e^{-kl''(m,n)}}{l''(m,n)} \sin\{kl''(m,n)\} \right] \right\rangle}{\sum_{n=0}^{\infty} \left\langle \left[\frac{e^{-kl''(0,n)}}{l''(0,n)} \cos\{kl''(0,n)\} \right] + 2 \sum_{m=1}^{\infty} \left[\frac{e^{-kl''(m,n)}}{l''(m,n)} \cos\{kl''(m,n)\} \right] \right\rangle}, \quad (12)$$

In precise measurement, the constant phase delay due to the effect of a silver paste is added to the Eq. (12). The in-plane thermal diffusivity and the out-of-plane thermal diffusivity are determined simultaneously by the curve fitting method, which is based on a simplex algorithm [11], where the entire Df vs. x curve is fitted to the Eq. (12).

3. PRELIMINALLY MEASUREMENT USING ISOTROPIC MATERIALS

The verification of the new method is evaluated by checking with the thermal diffusivities of the stainless steel (Standard Reference Material, SRM1461), which were obtained from the NIST, and pure copper. The detailed construction and operation of the apparatus are given in ref. [2, 4]. This apparatus permits in-plane thermal diffusivity measurement with an uncertainty of not more than $\pm 3.0\%$ [4]. The sample shape, experimental conditions and reference values of SRM1461 [12] and pure copper [13] are listed in Table I. Figure 2 shows the Df vs. x/d measurement results of SRM1461 and pure copper with fitting curves from Eq. (12). The deviations of the phase-lag for the experiments from the Eq. (12) are shown in Fig. 3. The deviations

are generally less than $\pm 0.4 \%$. The in-plane and the out-of-plane thermal diffusivities of SRM1461 and pure copper analyzed by a curve fitting are listed in Table II with a result of the in-plane thermal diffusivity calculated from the slope at the region (b) in Fig. 2. The in-plane thermal diffusivities a_{xy} of stainless steel and pure copper obtained from a curve fitting and a slope are in good agreement with recommended values within $\pm 2.6 \%$. The out-of-plane thermal diffusivities a_z were underestimated about 11 % and 52 %, respectively. The value of the out-of-plane thermal diffusivity is mainly determined by analyzing the information of the Df vs. x/d curve at the region (a) in Fig. 2, which is called a “thickness effect”. Around the origin, however, relative beam diameter becomes larger, and the assumption of the point heat source is not realized. That is why the out-of-plane thermal diffusivity has larger uncertainty. Additionally, the degree of the thickness effect around the origin is determined by the thermal thickness, i.e. $(a_{xy}/a_z) \cdot d$ and thermal wave number k defined as Eq. (3). Both the thickness and k value of the copper sample are smaller than those of the SRM1461 sample. That is why the pure copper sample has larger disagreement than the SRM1461 with the in-plane values. In the case of GS, though the k value is smaller than that of pure copper and SRM1461 samples, the thermal thickness of GS is larger than that of those samples due to its large anisotropy between xy and z directions. Therefore, measured out-of-plane thermal diffusivity value of GS would be underestimated 11 ~ 52 %.

4. RESULTS AND DISCUSSION

The sample shape of GS and the experimental conditions for thermal diffusivity measurement are listed in Table III. A series of seven measurement was

carried out with the change of the modulating frequency from 5.2 to 95.4 Hz. Figure 4 shows a typical example of the Δf vs. x measurement result at room temperature and fitting curve from Eq. (12) at 10.3 Hz. The deviation of the phase-lag for the measurement from the Eq. (12), which is shown at the bottom of the Fig. 4, is generally less than ± 0.5 %. Figure 5 shows the frequency dependence of the effective thermal diffusivity obtained from the fitting method. The analyzed thermal diffusivity has approximately constant values in the range $0.22 < 1/f^{1/2} < 0.44$, which corresponds to the thermal diffusion length ranging 3.5 to 7.0 mm, and is regarded as effective range. The average values of the in-plane and the out-of-plane thermal diffusivities in the effective range at room temperature are determined to be $a_{xy} = 798 \text{ mm}^2\text{s}^{-1}$, $a_z = 15.7 \text{ mm}^2\text{s}^{-1}$, respectively. The temperature dependence of the in-plane and the out-of-plane thermal diffusivities at the temperature range from 30 to 350 K are shown in Fig. 6. It is clear that both the in-plane and the out-of-plane thermal diffusivities have large temperature dependence. They have the maximum values around 100 K and 70 K, respectively. These values are approximately 7 and 10 times larger than the values at 350 K, respectively. It is also confirmed that GS has extreme thermal anisotropy in the in-plane direction and the out-of-plane direction. Figure 7 shows the anisotropy ratio a_{xy}/a_z of GS in the present temperature range. This ratio increases from 25 to 50 as the temperature rises, which means the value of the in-plane thermal diffusivity is about 25 ~ 50 times larger than that of the out-of-plane one.

5. CONCLUSIONS

The results can be summarized as follows:

- (1) A simultaneous measurement of the in-plane thermal diffusivity and the

out-of-plane thermal diffusivity by a laser-heating ac calorimetric method has been proposed.

- (2) The three-dimensional ac temperature response for anisotropy plate-like sample was numerically estimated using Green's function.
- (3) The verification is confirmed using isotropic materials at room temperature.
- (4) This method was applied to the graphite sheet measurement at the temperature range from 30 to 350 K, and large temperature dependence and extreme anisotropy of thermal diffusivity have been clarified quantitatively.

ACKNOWLEDGMENT

We would like to acknowledge Mr. N. Nishiki of Matsushita Electric Industrial Co., Ltd. for supplying graphite sheets. We would also like to thank Dr. M. Okaji and Mrs. K. Tomoda of National Research Laboratory of Metrology for many helps during this research.

REFERENCES

1. H. Nagano, H. Kato, A. Ohnishi, N. Nishiki and Y. Nagasaka, *Proc. 19th Jpn. Symp. Thermophys. Prop.*, Fukuoka, Japan (1998), pp. 247-250.
2. H. Nagano, H. Kato, A. Ohnishi and Y. Nagasaka, *High Temp.- High Press.* (to be published).
3. H. Nagano, H. Kato, A. Ohnishi, N. Nishiki and Y. Nagasaka, *Proc. 37th Natl. Heat Transf. Symp. Jpn.*, Kobe, Japan, May (2000). (to be published)
4. H. Kato, *Proc. 20th Jpn. Symp. Thermophys. Prop.*, Tokyo, Japan (1999), pp. 400-403.
5. Y. Gu and I. Hatta, *Jpn. J. Appl. Phys.*, **30**:1137 (1991).
6. I. Hatta, R. Kato and A. Maezono, *Jpn. J. Appl. Phys.*, **25**:L493 (1986).
7. T. Azumi, K. Takahashi, Y. Ichikawa, K. Motonari and K. Yano, *Proc. 8th Jpn. Symp. Thermophys. Prop.*, Japan (1987), pp. 171-174.
8. H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids*, 2nd ed., (Oxford University Press, New York, 1959), p. 263.
9. H. Kato, K. Nara and M. Okaji, *Proc. 4th Asian Thermophys. Prop. Conf.*, Tokyo, Japan (1995), pp. 581-584.
10. C. A. Bennett, JR., and R. R. Patty, *Appl. Opt.*, **21**:49 (1982).
11. J. A. Nelder and R. Mead, *Comp. J.*, **7**:308 (1965).
12. S. H. Lee, T. Terai, Y. Takahashi, *Jpn. J. Thermophys. Prop.*, **8**:213 (1994).
13. Y. S. Touloukian, R. W. Powell, C. Y. Ho and P. G. Kelemens, *Thermophysical Properties of Mater* 1, IFI/PLENUM, New York - Washington (1970), p. 81.

Table I. Shape of Samples and Experimental Conditions.

Sample	Thickness [mm]	Shape [mm]	Frequency [Hz]	Scanning Length [mm]	Reference Value [mm ² Å ⁻¹]
SRM1461	0.5	$\varnothing 12$	2.11	2.0	3.72 [12]
Pure Copper	0.1	12×12	28, 33	0.4	117 [13]

Table II. Thermal Diffusivity Values of Stainless Steel and Pure Copper

Obtained from a Fitting Method and a Slope.

Sample	Frequency [Hz]	Fitting	Fitting	Slope	Standard
		(in-plane)	(out-of-plane)	(in-plane)	Deviation
		[mm ² Is ⁻¹]	[mm ² Is ⁻¹]	[mm ² Is ⁻¹]	[%]
SRM1461	2.11	3.70	3.36	3.73	0.180
	2.11	3.69	3.28	3.69	0.089
Pure Copper	28	119	57.4	114	0.078
	33	118	56.6	114	0.080

Table III. Shape of GS Sample and Experimental Conditions.

Sample	Thickness	Shape	Scanning	Temperature
	[mm]	[mm]	Length	[K]
			[mm]	
Graphite Sheet	0.1	7×40	4.0	30 ~ 350

FIGURE CAPTIONS

- Fig. 1. Sample shape for thermal diffusivity measurement (a) and mirror images of point heat source in the y direction (b) and in the z direction (c).
- Fig. 2. Example of the measured phase-lag vs. nondimensional distance and fitting curves of SRM1461 and pure copper.
- Fig. 3. Deviations of measured phase-lag from fitting curves given by Eq. (12) of SRM1461 and pure copper.
- Fig. 4. Typical phase-lag vs. distance data and fitting curve given by Eq. (12) of GS at room temperature. Deviation of the experimental data from fitting curve is displayed at the bottom of the figure.
- Fig. 5. Frequency dependence of effective thermal diffusivity for GS at room temperature.
- Fig. 6. Temperature dependence of in-plane and out-of-plane thermal diffusivities of GS.
- Fig. 7. Anisotropy ratio of in-plane thermal diffusivity to out-of-plane thermal diffusivity for GS.













